Electron capture dissociation of peptide hormone changes upon opening of the tocin ring and complexation with transition metal cations

Y.E.M. Van der Burgt, M. Palmblad, H.C. Dalebout, R.M.A. Heeren, A.M. Deelder

Rapid Comm. Mass Spectrom. 2009, 23, 31-38

Electron capture dissociation (ECD) is an analytical technique in mass spectrometry (MS) that allows detailed structural study of biomolecules to gain insight in their function. In this work the ECD behavior of two peptide hormones oxytocin (OT1) and vasopressin (VP1) was studied. The results of OT1 and VP1 were compared to structural analogues OT2 and VP2, which have similar amino acid sequences but lack the tocin ring. The ECD results showed that both the fragment type (c/z versus b/y) and the cleavage sites (ring versus tail) changed upon opening of the tocin ring. All four peptides were complexed with three different transition metal cations (Zn(2+), Ni(2+) and Cu(2+)) and the ECD results were compared to those obtained from the doubly protonated species. The use of various metal ions yielded different cleavages sites within the same peptide. This can be an effect of the metal ion itself, or a consequence of a change in conformation as was suggested earlier. In addition, the type of fragment ion varied for each metal-complexed peptide, which is in agreement with previous observations.